

MOLECULAR SIEVE PROPERTIES OF ACTIVATED ANTHRACITE

J. E. Metcalfe, III, M. Kawahata, and P. L. Walker, Jr.

Fuel Technology Department
The Pennsylvania State University
University Park, Pennsylvania

Introduction

It is well known that coals exhibit molecular-sieve properties. Such properties are characterized by much higher $n\text{-C}_4\text{H}_{10}$ adsorption than $\text{iso-C}_4\text{H}_{10}$ adsorption at room temperature (1) and particularly by activated adsorption of N_2 and A at 77°K . (1, 2, 3, 4, 5). However, this molecular-sieve behavior in the case of raw coal is of little practical value, since the diffusion rate of the adsorbate into the pore system is usually very slow and the total adsorption capacity is usually very low.

There is an increasing interest and use, today, of molecular-sieve materials by the petroleum industry for the separation of straight from branched-chain hydrocarbons. Synthetic crystalline zeolites are being used almost exclusively for this purpose (6). Charcoals made from the pyrolysis of certain polymers show promise (7). In this paper, the possibilities of producing a suitable molecular-sieve material by the activation of anthracite is considered.

Experimental

Anthracite Used - A Pennsylvania anthracite, which was ground in a fluid energy mill to an average particle size of 6μ on a weight basis, was used in this study. The proximate analysis (air-dry basis) of the anthracite was: moisture, 1.2%; V. M., 8.2%; fixed C, 79.4%; and ash, 11.2%.

Devolatilization of the Anthracite - Prior to activation, the anthracite was devolatilized in a N_2 atmosphere at 950°C . for 6 hours. No attempt was made to analyze the product gases during devolatilization; but from previous studies on kinetics of volatile matter release from anthracite, most of the gas released was H_2 (8).

Activation of Anthracite - Because of the fine particle size of anthracite used, a down-flow fixed bed reactor was employed. The reactor, which was 2.25 in. i. d., 3.25 in. o. d., and 2 ft. long, was made of 10-18 steel tubing. The anthracite sample holder, which could be inserted into the reactor, was 304 stainless steel. Its dimensions were 1.87 in. i. d., 0.065 in. wall thickness, and 17 in. long. The bottom was perforated to allow for the passage of the gases. Gas mixing and preheater sections were present, before the reactor. The entire apparatus is described in detail elsewhere (9).

For a run, an oven dried sample of anthracite of known weight was placed in the sample holder. The sample was heated to activation temperature in N_2 and then reacted with a 90% CO_2 -10% CO gas mixture, at a total pressure of 1 atm. Following reaction, the sample was cooled in N_2 and the percentage burn-off measured from the loss in sample weight. Carbon monoxide was added to the inlet stream so that more uniform activation through the bed would occur. That is, it minimized the effect of small amounts of product CO strongly retarding the gasification reaction (10).

Apparatus to Measure Properties of Anthracite

Apparent density - The apparent density of the samples was determined by Hg displacement. A Hg porosimeter was used (11), in which the total pressure above the Hg was raised to 2,000 psi. At this pressure, Hg is forced into openings greater than ca. 1000 Å. Therefore, it is expected that the voids between anthracite particles were completely filled. At the same time, the volume of Hg forced into pores above 1000 Å. within the anthracite particles is thought to be negligible (12).

Helium density - Prior to the measurement, the samples were outgassed at 125°C. for 8 hours. The He densities were determined by the conventional method in which a measured quantity of He was expanded into a sample holder (held at 30°C.) of known volume containing a sample of known weight. A 30 min. period was found adequate to reach equilibrium.

Adsorption apparatus - A static adsorption apparatus of the typical design (13), containing Hg float valves, was used. All adsorption studies were conducted at $30 \pm 0.1^\circ\text{C}$. Prior to measuring the free space with He, the samples were outgassed at 250°C. for 7 hours. Because of the very slow diffusion of the hydrocarbon adsorbates into the raw and devolatilized anthracites, 24 hours was allowed to reach equilibrium for each adsorption point. For the activated samples, a one hour equilibration time was found sufficient. The adsorbates used, $n\text{-C}_4\text{H}_{10}$, $\text{iso-C}_4\text{H}_{10}$, and $\text{neo-C}_5\text{H}_{12}$, were obtained from the Matheson Co. and were of greater than 99.9% purity.

Results and Discussion

It was decided to activate anthracite of micron size in this study in order to attain the optimum in uniform particle activation and to decrease adsorption equilibration time to a minimum. Walker and co-workers (14) discuss the effect of particle size on non-uniformity of gasification. Kawahata and Walker (12) show that the specific pore volume of activated anthracite increases with decreasing particle size in the range 16 to 150 mesh.

Unfortunately, however, the handling of 6 μ anthracite during activation proved to be a problem. Initially, activation in a fluid bed apparatus, which was previously used successfully to react 100x150 mesh anthracite (15), was attempted. Excessive carry-over of the anthracite from the reactor as a result of continuous agglomeration and de-agglomeration made the use of fluidization impractical. In the case of the down-flow fixed bed reactor which was used for activation, it became evident that channeling of the gas was a problem. This apparently resulted in non-uniform reaction through the bed. That is, from the total per cent burn-off and the change in apparent density of anthracite during a run, the fraction of activation which took place within the anthracite particle (as opposed to removing external volume and thereby decreasing particle size) could be estimated. For the seven activation runs made, the percentage of internal activation varied widely, up to 100%, with no trend being found with changing activation temperature between 750 and 840°C. Results for only the sample with 100% internal activation are given here, to show under the best conditions what type of molecular-sieve properties activated anthracite can have.

The activated sample to be considered here, was reacted at 840°C. for 23.5 hours to 34.8% burn-off. Figure 1 shows the isotherms for the adsorption

of hydrocarbons on this sample. The isotherms can be closely approximated by the Langmuir equation, from which monolayer adsorption volumes can be estimated. These volumes for the activated and raw anthracite are given in Table I. Monolayer volumes for the devolatilized anthracite are not given, since they were very small and could not be accurately measured. For $n\text{-C}_4\text{H}_{10}$ adsorption at a relative pressure of 0.3, the volume adsorbed on the devolatilized anthracite was roughly 10% of that adsorbed on the raw anthracite. This indicates significant closure and contraction of pores upon heating of the raw anthracite to 950°C . Such a result has been previously reported upon the heat treatment of bituminous chars to higher temperatures (16).

From Table I, it is seen that the area available to the hydrocarbons is sharply increased upon activation, as expected. Of more importance, is the fact that the adsorption rate is markedly increased and that wide differences in the pore area available to the hydrocarbons still exist.

Table II summarizes the results for the apparent and He densities and total open pore volume on a m.m.f.b. To place the density results on a m.m.f.b., the apparent and He density of the mineral matter in all samples was taken as 2.7 g./cc. (17). The total open pore volume is considered to be the volume in pores $< 1000 \text{ \AA}$ and $> 2.5 \text{ \AA}$ in diameter. The lower limit is set by the size of pore into which He can diffuse at a significant rate at 30°C . (18).

On the basis of these results, the nature of the molecular pore system in the anthracites can be clarified further. From Hg porosimeter data on anthracite activated to 38% burn-off, it has been shown that about 94% of the total open pore volume is located in pores $< 28 \text{ \AA}$ in diameter (12). According to the Kelvin equation, pores of up to ca. this diameter will be filled by the hydrocarbons studied at a relative pressure of 0.3. Therefore, the assumption is made that the volumes of hydrocarbon adsorbed at a relative pressure of 0.3 are located in pores between a lower limit (below which the hydrocarbon will not enter) and 1000 \AA . Then, by subtracting these pore volumes from the total open pore volume, distribution data in the molecular pore size range can be determined. In agreement with Breck and co-workers (19) and others, the minimum effective pore size into which a hydrocarbon can penetrate is taken as the diameter of the circumscribed circle of minimum cross-sectional area of the hydrocarbon molecule. These minimum dimensions are 4.9, 5.6, and 6.5 \AA for $n\text{-C}_4\text{H}_{10}$, $\text{iso-C}_4\text{H}_{10}$, and $\text{neo-C}_5\text{H}_{12}$, respectively.

These results are summarized graphically in Figure 2. It is seen that even though the total open pore volume is increased on devolatilization (presumably by volatile matter release unblocking pores), the amount of pore volume available to $n\text{-C}_4\text{H}_{10}$ and larger hydrocarbons sharply decreases. Comparing the volume distributions for the raw with the activated anthracite, it is seen that in spite of a large increase in total pore volume upon activation, the pore volume between 2.5 and 4.9 \AA has decreased. This would suggest that there is little pore volume below 4.9 \AA to be opened up by additional burn-off of this anthracite. It is to be emphasized that the volume reported below a minimum effective pore size would be expected to increase with increasing adsorption temperature, because of activated diffusion and an increasing magnitude of vibration of the atoms around a pore opening.

It is of interest to compare the activated anthracite with Type A synthetic zeolite pellets for adsorption of $n\text{-C}_4\text{H}_{10}$ and $\text{iso-C}_4\text{H}_{10}$ (19). At room temperature, the 5A zeolite has a capacity of ca. 50 cc. $n\text{-C}_4\text{H}_{10}$ /g. (S.T.P.) and 2 cc. $\text{iso-C}_4\text{H}_{10}$ /g. It is thought that the adsorption of

iso-C₄H₁₀ primarily occurs on the clay binder holding the small zeolite particles together in the pellet. The ratio of gases adsorbed is ca. 25. In contrast, the activated anthracite has a capacity of ca. 110 cc. n-C₄H₁₀/g. (m.m.c.b.) and 40 cc. iso-C₄H₁₀/g. The ratio of gases adsorbed is ca. 2.8. Pelletizing the anthracite for use in fixed bed operations would be expected to lower both the adsorption capacities and separation ratio. It is obvious, then, that this activated anthracite sample does not show the sharp molecular sieve effect demonstrated by the zeolite. This is to be expected, since a range of molecular pore sizes is present in the raw and activated anthracite. Nevertheless, because of the relatively low cost of activated anthracite, it may have possible applications for rough separations in conjunction with zeolites.

Acknowledgment

We wish to acknowledge the financial support of the Coal Research Board of the Commonwealth of Pennsylvania for making this research possible.

References

1. R. B. Anderson, W. Keith Hall, J. A. Lecky, and K. C. Stein, *J. Phys. Chem.*, **60**, 1548 (1956).
2. P. Le R. Malherbe, *Fuel*, **30**, 97 (1951).
3. F. A. P. Maggs, *Nature*, **169**, 793 (1952).
4. S. J. Gregg and M. I. Pope, *Fuel*, **38**, 501 (1959).
5. D. W. Van Krevelen and J. Schuyer, "Coal Science", Elsevier Publ. Co., 1957, pp. 129-136.
6. R. A. Jones, "Advances in Petroleum Chemistry and Refining", Interscience Publishers, Inc., 1961, pp. 115-161.
7. J. R. Dacey and D. G. Thomas, *Trans. Faraday Soc.*, **50**, 740 (1954).
8. Jean Worrall and P. L. Walker, Jr., "The Isothermal Kinetics of Volatile Matter Release from Anthracite", Coal Research Board of Pennsylvania Special Report 16, 1959.
9. J. E. Metcalfe, III, M.S. Thesis, The Pennsylvania State University, 1962.
10. J. Gadsby, F. J. Long, P. Sleightholm, and K. W. Sykes, *Proc. Royal Soc.*, **193A**, 357 (1948).
11. P. L. Walker, Jr., F. Rusinko, Jr., and E. Raats, *J. Phys. Chem.*, **59**, 245 (1955).
12. M. Kawahata and P. L. Walker, Jr., "Mode of Porosity Development in Activated Anthracite", Proceedings of the Fifth Carbon Conference, in press.
13. P. H. Emmett, *ASTM Tech. Publ.* 51, pp. 95-105 (1941).
14. P. L. Walker, Jr., F. Rusinko, Jr., and L. G. Austin, "Advances in Catalysis", Academic Press, 1959, Vol. 11, pp. 133-221.
15. M. Kawahata and P. L. Walker, Jr., Proceedings of the Anthracite Conference, Mineral Industries Bulletin 75, The Pennsylvania State University, 1960, pp. 63-78.
16. R. L. Bond and D. H. T. Spencer, Proceedings of the Third Carbon Conference, Pergamon Press, 1957, pp. 357-365.

17. A. M. Wandless and J. C. Macrae, *Fuel*, 13, 4 (1934).
18. R. E. Franklin, *Fuel*, 27, 46 (1948).
19. D. W. Breck, W. G. Eversole, R. M. Milton, T. B. Reed, and T. L. Thomas
J. Am. Chem. Soc., 78, 5963 (1956).

Table I

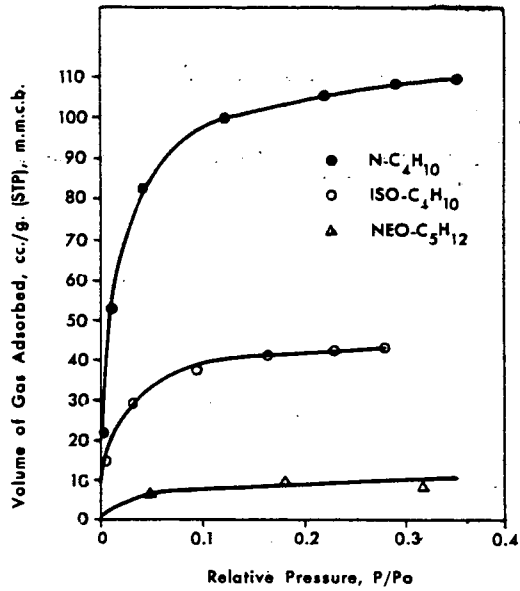
Monolayer Volumes for Different Hydrocarbons
on Raw and Activated Anthracite (m.m.f.b.)

	V_m , cc./g. (S.T.P.)		
	<u>n-C₄H₁₀</u>	<u>iso-C₄H₁₀</u>	<u>neo-C₅H₁₂</u>
Raw	12.6	8.6	2.3
Activated	134	54.5	15.5

Table II

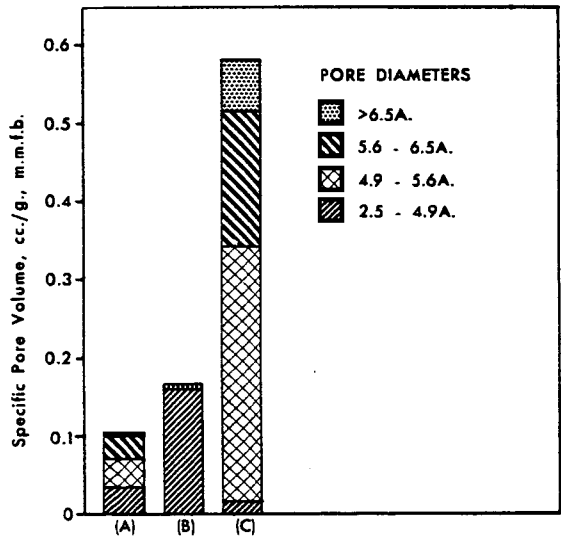
Densities and Total Open Pore Volume in Raw,
Devolatilized, and Activated Anthracite (m.m.f.b.)

	<u>App. Density</u> <u>g./cc.</u>	<u>He Density</u> <u>g./cc.</u>	<u>Total Open Pore</u> <u>Volume cc./g.</u>
Raw	1.24 ₅	1.43 ₈	0.10 ₈
Devolatilized	1.51 ₀	2.01 ₀	0.16 ₅
Activated	0.95 ₇	2.15 ₆	0.58 ₁



HYDROCARBON ADSORPTION AT 30°C.
ON ANTHRACITE ACTIVATED TO 34.8%
BURN-OFF AT 840°C.

Figure 1



PORE VOLUME DISTRIBUTIONS IN RAW
(A), DEVOLATILIZED (B) AND ACTIVATED
(C) ANTHRACITES

Figure 2